Experimental study and modelling of thermal runaway: Application to dichromate catalysed hydrogen peroxide decomposition

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Abstract

This paper deals with the thermal runaway of exothermic dichromate catalysed hydrogen peroxide decomposition. This reaction is characterized by a kinetic law which presents two limiting cases: zeroth and second apparent kinetic order in peroxide so that classical stability conditions could not be directly applied. A thermal stability criterion is proposed and applied to performed and simulated batch experiments. Some classical runaway boundaries are compared, and a condition, based on the Morbidelli's condition is proposed. The characteristics of zeroth order reactions, whose stability conditions have to be verified not only for initial conditions, but also throughout the reaction, are also illustrated.
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1. Introduction

Study and application of safety conditions in chemical processes is significantly increasing especially since a series of accidents with height media repercussions occurred in industrial plants. Batch processes represent the more hazardous processes, from the thermal runaway point of view. Indeed, statistics show that 60% of thermal runaways occur in fine chemistry, plastics and resins industry or manufacture of basic organic materials [1].

Study of safety conditions in chemical processes has been the subject of many theoretical studies [2–4], dealing particularly with thermal runaway of reactors. However, few experimental examples were published up to now [5–7].

Runaway boundaries detailed in literature are generally proposed for reactions of given kinetic order. In the case of reactions whose kinetic law cannot be reduced to a simple model of N-order reaction, adequate correlations cannot be found. In this paper, we propose an experimental study of thermal runaway and control of an exothermic homogeneous catalytic reaction: the decomposition of hydrogen peroxide by potassium dichromate.

2. Dichromate catalysed hydrogen peroxide decomposition

The dichromate catalysed hydrogen peroxide decomposition reaction has the following advantages:

- it is a reaction of easy implementation,
- it has an "adjustable exothermicity" obtained in varying the hydrogen peroxide concentration,
- it uses non-toxic reactants and products, which minimizes the consequences in the case of thermal runaway.

This reaction was the subject of some previous studies [8–10] and involves the following stoichiometric mechanism:

$$2H_2O_2 + Cr_2O_7^{2-} \xleftrightarrow{K} Cr_2O_9^{2-} + 2H_2O,$$

$$Cr_2O_9^{2-} \xrightarrow{k'} Cr_2O_7^{2-} + O_2$$
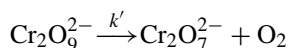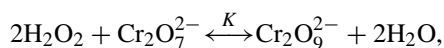
It is supposed that the first reactional stage is fast and balanced, and the second slower one constitutes the determining kinetic stage [11]. Equilibrium constant K and reaction rate r_{cr}

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Nomenclature

A	heat transfer area (m^2)
C_0	initial hydrogen peroxide concentration (mol l^{-1})
C_p	specific heat capacity (J kg^{-1} K^{-1})
E	activation energy (J mol^{-1})
F	flow (mol s^{-1})
$\Delta_r H$	enthalpy of reaction (J mol^{-1})
k	rate constant (s^{-1})
k_0	frequency factor (s^{-1})
K	equilibrium constant (L^2 mol^{-2})
m	mass (kg)
n	kinetic order
n_j	moles of component j (mol)
P	power (W)
P_v	pression vapor
r	reaction rate (mol L s^{-1})
T	temperature (K)
ΔT_{ad}	adiabatic temperature rise (K)
U	overall heat transfer coefficient (W m^{-2} K^{-1})
V	volume (L)
X	reactant extent

Greek letters

Γ	molar heat capacity (J mol^{-1} K^{-1})
ν_j	stoichiometric coefficient of component j
τ_c	thermal constant (s)
φ	thermal inertia

Subscripts

ad	adiabatic
amb	ambient
calc	calculated
crit	critical
exp	experimental
g	gas
max	maximal value
reactants	reactant
reactor	reactor
th	theoretical
v	vapor
w	wall
0	initial

can be expressed as follows:

$$K = \frac{[Cr_2O_9^{2-}][H_2O]^2}{[Cr_2O_7^{2-}][H_2O_2]^2}, \qquad r_{Cr} = k'[Cr_2O_9^{2-}] \qquad (1)$$

Defining K' as:

$$K' = \frac{K}{[H_2O]^2} \qquad (2)$$

the consumption rate of dichromate, which is half of that of peroxide, can finally be expressed as:

$$r_{H_2O_2} = 2r_{Cr} = 2k'[Cr_2O_9^{2-}]$$

$$= k[Cr_2O_9^{2-}] = k\frac{K'[H_2O_2]^2[Cr_2O_7^{2-}]_0}{1 + K'[H_2O_2]^2} \qquad (3)$$

A preliminary kinetic study [12] allowed determining the kinetic and thermodynamic parameters of reaction:

$$k = 1.39 \times 10^9 \exp\left(-\frac{6600}{T}\right) \text{ s}^{-1},$$

$$\Delta_r H = -94 \text{ kJ mol}^{-1},$$

$$K' = \exp\left(\frac{2768}{T} - 5.16\right) \text{ L}^2 \text{ mol}^{-2}$$

According to the peroxide concentrations, the apparent order in peroxide presents two limiting cases: zeroth order for high concentrations in peroxide, and second order for the weakest concentrations.

$$K'[H_2O_2]^2 \gg 1 \rightarrow r = k[Cr_2O_7^{2-}]_0,$$

$$K'[H_2O_2]^2 \ll 1 \rightarrow r = kK'[H_2O_2]^2[Cr_2O_7^{2-}]_0 \qquad (4)$$

In our experimental conditions, the initial concentration of peroxide (included between 1 and 3 mol l^{-1}) are high enough so that the apparent order can be considered equal to zero for conversion up to 90%.

3. Experimental study

The study was carried out in isoperibolic mode, in a batch heat jacketed reactor with constant wall temperature T_w. A sketch of the experimental setup is presented in Fig. 1.

3.1. Protocol

The reactants were purchased from Prolabo and were used as received. The purity of the potassium dichromate is higher than 99.9% and the concentration of hydrogen peroxide is 9.82 M (110 V). Two separated potassium dichromate and hydrogen peroxide solutions were prepared. Volumes of these solutions
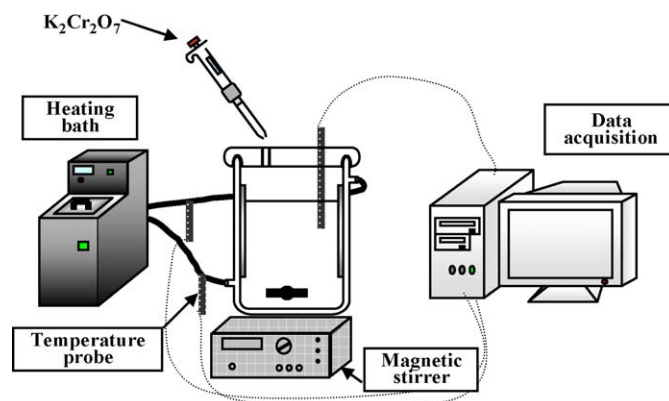

Fig. 1. Experimental setup.

were selected to keep a total final volume of 0.15 l and to obtain defined concentrations after mixture. The hydrogen peroxide solution was first loaded, and agitated at 700 rpm. Once the desired initial temperature was reached, the dichromate solution was rapidly added using a micropipette. The dichromate concentration is much lower than that of peroxide, so the dichromate volume is small compared to that of peroxide (less than 3%) and its dispersion in the solution can be considered as instantaneous. Agitation was continuously ensured by a magnetic stirrer whose stirring speed was maintained at 700 rpm.

The temperature variation versus time was finally recorded, with an acquisition rate of 10 points per second.

3.2. Modelling

The kinetic model presented in the previous section can describe the reactor temperature evolution according to mass and heat balances.

3.2.1. Thermal characterization

The thermal characteristics of the reactor are determined using a traditional calorimetric measurement method. The procedure consists in heating the reactor contents by a thermal source (electric resistance of known power) and to follow the temperature evolution against time. The determined thermal characteristics are here:

- the overall heat transfer coefficient U, which accounts for the eventual heat losses,
- the thermal inertia φ such as $\varphi = 1 + (m_{reactor}C_{p_{reactor}}/m_{reactants}C_{p_{reactants}})$, which accounts for the reactor's heat capacity, such that φ is the ratio of the total heat flow necessary to heat the reactants and the reactor, to the reactants heat flow.

Defining T_w as the cooling liquid temperature, P as the power of a thermal source and A as the heat transfer area, that is to say the measured wet area in contact with the reactor walls, the resolution of heat balance in batch mode [13] allows the determination of the thermal characteristics:

$$UA(T_w - T) = m_{reactants}C_{p_{reactants}}\varphi\frac{dT}{dt} - P \tag{5}$$

Resolution of Eq. (5) was numerically performed using Matlab®. The least square difference between calculated and measured temperatures was minimized using the subroutine 'fminsearch' that finds the minimum of a function of several variables, making it possible to identify the two parameters U and φ.

This study allowed estimating the overall heat transfer coefficient UA to 5.97 W K^{-1}, and the thermal inertia φ to 1.057.

3.2.2. Mass and heat balances

For a reaction implemented in batch mode, the mass balance leads to:

$$\frac{dn_j}{dt} = v_j r V \tag{6}$$

The hydrogen peroxide decomposition releases some oxygen and the reactional volume could then vary as reaction proceeds. In addition, for high temperatures, the evaporation of components involves mass and heat losses. However, as can be seen in Appendix A, the evaporation mass loss remains negligible, so that the reactional volume can be thought as constant.

It has been choosen to define reactant extent, X, according to hydrogen peroxide, since dichromate is regenerated as reaction proceeds, as shown by the reactional mechanism.

$$n_{H_2O_2} = n_{H_2O_2,0}(1 - X) \tag{7}$$

Finally, the mass balance is given by the following equation:

$$rV = -\frac{dn_{H_2O_2}}{dt} = n_{H_2O_2,0}\frac{dX}{dt} = [H_2O_2]_0 V_0 \frac{dX}{dt} \tag{8}$$

Taking into account the evaporated heat flow, which is related to the evaporation of reactional medium components, the heat balance is given by:

$$UA(T_w - T) = mC_p\frac{dT}{dt} + rV\Delta_r H + F_{O_2}\Gamma_{p,O_2}(T - T_{amb})$$
$$+ \sum_i \frac{dn_{i,g}}{dt}\Delta H_{vap,i} \tag{9}$$

According to the following assumptions:

- The evaporation term of chromium is supposed to be negligible, since the chromium concentration is far lower than that of water.
- The evaporation of peroxide is supposed to be negligible compared to that of water, since the vaporization pressure of peroxide P_{vap,H_2O_2} is very low compared to that of water P_{vap,H_2O}.
- It is supposed that the released oxygen is saturated with water and that the output flow, which consists of oxygen and vapor of water, is in steady state. The evaluation of the evaporated water flow is presented in Appendix A.

The heat balance can then be simplified into:

$$UA(T_w - T) = mC_p\frac{dT}{dt} + rV\left(\Delta_r H + \frac{1}{2}\Gamma_{p,O_2}(T - T_{amb})\right.$$
$$\left. + \frac{1}{2}\frac{P_{vap,H_2O}}{P_{atm} - P_{vap,H_2O}}\Delta H_{vap,H_2O}\right) \tag{10}$$

Defining τ_c as a characteristic thermal constant:

$$\tau_c = \frac{m_{reactants}C_{p_{reactants}}}{UA} \tag{11}$$

and ΔT_{ad} as the adiabatic temperature rise:

$$\Delta T_{ad} = -\frac{[H_2O_2]_0(-\Delta_r H)}{\rho_{reactants}C_{p_{reactants}}} \tag{12}$$

Table 1
Experimental conditions and parameters

Experiment	$[H_2O_2]_0$ (M)	$[Cr_2O_7]_0$ (M)	T_0 (K)
1	1.8	0.003	303
2	2.7	0.003	303
3	6	0.003	303
4	1.8	0.003	313
5	2.7	0.003	313
6	6	0.003	313
7	1.8	0.003	323
8	2.7	0.003	323
9[a]	6	0.003	323
10	1.8	0.03	303
11[a]	2.7	0.03	303
12[a]	6	0.03	303
13	1.8	0.03	313
14[a]	2.7	0.03	313

[a] Simulated results.

The heat balance is finally:

$$\frac{dT}{dt} = \frac{T_w - T}{\tau_c \varphi} + \frac{\Delta T_{ad}}{\varphi} \left(1 + \frac{1}{2} \frac{\Gamma_{p,O_2}}{\Delta_r H} (T - T_{amb}) \right.$$
$$\left. + \frac{1}{2} \frac{P_{vap,H_2O}}{P_{atm} - P_{vap,H_2O}} \frac{\Delta H_{vap,H_2O}}{\Delta_r H} \right) \frac{dX}{dt} \qquad (13)$$

3.3. Experimental study

Table 1 presents the performed experiments. The studied parameters are the initial potassium dichromate concentration, the hydrogen peroxide concentration and the initial reactants temperature, equal to the cooling liquid temperature. It will be possible, using this large number of experimental data, to study and define thermal runaway conditions. The stable tests are characterized by moderate temperature rises while unstable tests are characterized by thermal runaways.

Simulations, using Eqs. (8) and (13), showed in a preliminary way that Experiments 9, 11, 12, 14 could lead to significant thermal runaways. For this reason, the experiments were not carried out and only simulations results were used. This is justified by the fact that the model gives a very good description of the performed experiments, as can be seen in Fig. 2, presenting the reaction temperature for Experiments 5 and 6. Indeed the relative standard deviation is 1.9×10^{-3} and the mean absolute difference is 0.52 K [12].

4. Parametric sensitivity

4.1. Methodology

It can be noticed, in Fig. 2 that Experiment 5, characterized by a slight temperature rise, remains stable in case of variation of controls. It can be seen that Experiment 6 begins in a stable way with the same shape of the Experiment 5 curve, but when t exceeds 400 s, the curve's shape changes and the rate of temperature variation increases, inducing a thermal runaway of the reaction.
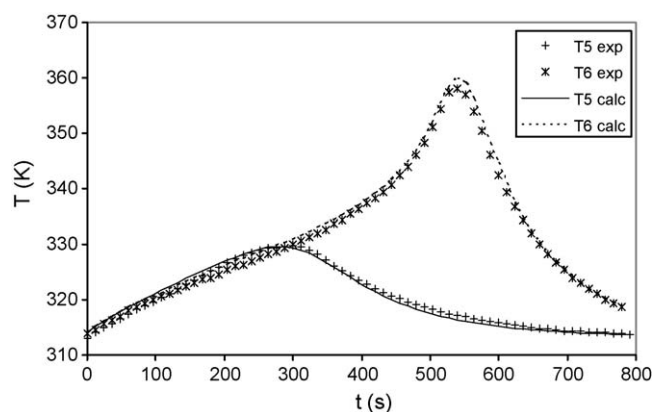

Fig. 2. Temperature evolution against time. T5 and T6 correspond to the experiments number 5 and 6.

This experimental observation leads to the definition of a thermal stability condition which states that the temperature increases without acceleration during the reaction, i.e. the temperature variation decreases against time.

Thus, the absence of any thermal runaway risk is ensured by the following condition:

$$\frac{dT}{dt} \geq 0 \quad \text{and} \quad \frac{d^2T}{dt^2} \leq 0$$

Graphically this condition requires the absence of any inflection point in the increasing part of the temperature variation against time. The thermal explosion is avoided if the temperature variation against time does not present any change of concavity during the temperature rise. Indeed if the concavity of the thermal profile is turned upwards, there is a temperature variation acceleration, and therefore a potential hazard in the case of breakdown of the cooling system. Under these conditions, Experiment 5 (presented in Fig. 2) is stable, whereas Experiment 6 is unstable, in case of variation of controls. This definition might be seen as restrictive, but has however the advantage to be easily observable and to allow defining a potential hazard.

Applying this definition, the performed experiments are reported in Fig. 3, on the diagram proposed by Villermaux [13] and Froment and Bischoff [14]. The squares represent the stable experiments, while the triangles represent the unstable ones.
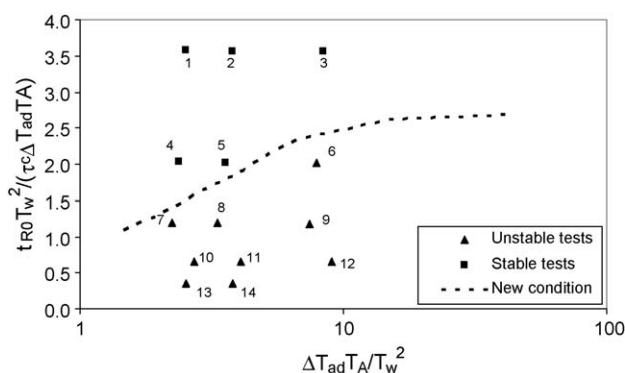

Fig. 3. Sensitivity diagram.

To better define the limit between the stable and unstable zones, we adopted a pseudo experimental methodology, based on the following approach. We simulated a very great number of tests with varying operating conditions. For each test, the thermal profile inside the reactor was plotted and the experimental definition of stability was applied. The precise limit between the stable and unstable zones is then plotted in dotted line in Fig. 3.

The proposed stability condition is compared with classical runaway boundaries in the next section.

4.2. Comparison with the classical thermal stability correlations

4.2.1. Characteristic numbers

In isoperibolic mode, the simplified heat and mass balances without any solvent evaporation are written:

$$UA(T_w - T) = m_{reactants} C_{p_{reactants}} \varphi \frac{dT}{dt} + rV\Delta_r H \quad (14)$$

$$\frac{dX}{dt} = \frac{r}{C_0} \quad (15)$$

The specific heat released by the reaction is proportional to:

$$q_r = \Delta T_{ad} \frac{dX}{dt} = \frac{\Delta T_{ad}}{t_R} \quad (16)$$

Whereas the specific heat transferred through the jacket is proportional to:

$$q_c = \frac{T - T_w}{\tau_c} \quad (17)$$

For a stable operation, the cooling system must transfer heat out of the reactor faster than it is produced in the reactor by the reaction. Therefore q_c must increase more quickly against temperature than q_r:

$$\frac{\partial q_C}{\partial T} \gg \frac{\partial q_r}{\partial T} \quad (18)$$

Thus

$$\frac{T_A \Delta T_{ad}}{T^2} \ll \frac{t_R}{\tau_c} \quad \text{with } T_A = \frac{E}{R} \quad (19)$$

This last relation is used as a basis of many thermal stability conditions published in the literature. Frequently, the two factors, t_R/τ_c comparing the reaction time with the thermal transfer time, and the thermal reaction number $(\Delta T_{ad} T_A)/T^2$, which represents a direct measurement of potential risk of the studied chemical process [1], are compared. These two factors are however always compared for initial conditions.

Since the studied reaction can be seen with an apparent zeroth order in peroxide until high conversion extents, we propose to compare our experimentally established thermal stability condition with correlations resulting from literature, for varying orders.

4.2.2. Criteria for zeroth order reactions

- Semenov studied an exothermic reaction system of zeroth order where the reactants were supposed as not consumed
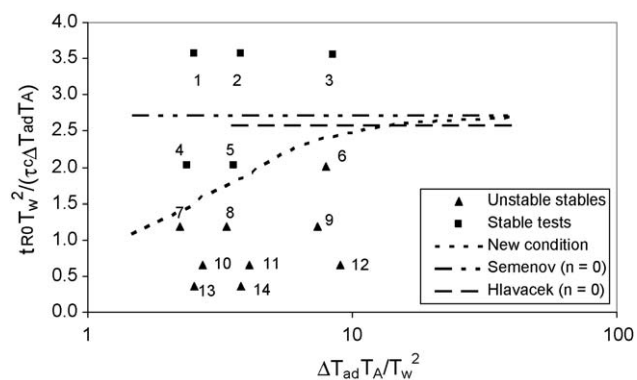

Fig. 4. Comparison of thermal stability criteria for zeroth order reactions.

[15]. Semenov defined a criterion (Semenov number) and a thermal stability condition which correspond to:

$$Se = \frac{T_A \Delta T_{ad}}{T_w^2} \frac{\tau_c}{t_{R0}} \quad (20)$$

$$Se \leq e^{-1} \quad \text{and} \quad T - T_w \leq \frac{T_w^2}{T_A} \quad (21)$$

This condition is very restricting. For example, for the studied system at $T_w = 303$ K, the temperature rise should not exceed 15 K. The Semenov condition, presented in Fig. 4, results in supposing some experiments as unstable whereas their realisation did not involve any thermal runaway.

- Hlavacek et al. [16] proposed a thermal stability condition for the reactions of zeroth order, whose expression is:

$$\frac{t_{R0}}{\tau_c} > \frac{1}{(1 + (T_0/T_A)\theta_{crit})^2} \exp\left(\frac{\theta_{crit}}{1 + (T_0/T_A)\theta_{crit}}\right) \quad (22)$$

where θ_{crit} represents the maximum authorised reduced temperature:

$$\theta_{crit} = \frac{T_{max}}{T_0} = \frac{1}{2} \left(\frac{T_A}{T_0}\right)^2 \left(1 - 2\frac{T_0}{T_A} - \left(1 - 4\frac{T_0}{T_A}\right)^{1/2}\right) \quad (23)$$

and T_0 the initial temperature.

According to this condition, the maximum authorised temperature rise for a stable reaction is about 30 K for our system. This relation is also presented in Fig. 4. The curve is very close to that obtained with the relation of Semenov. The stability condition proposed by Hlavacek also over-estimates the potential hazards.

Correlations for first order reactions are presented in the next section.

4.2.3. Criteria for first order reactions

- Hlavacek also proposed a semi-empirical relation for reactions of first order. This condition gives similar results to others correlations proposed in literature [17,18]. We have chosen to present the correlation of Hlavacek as an example:
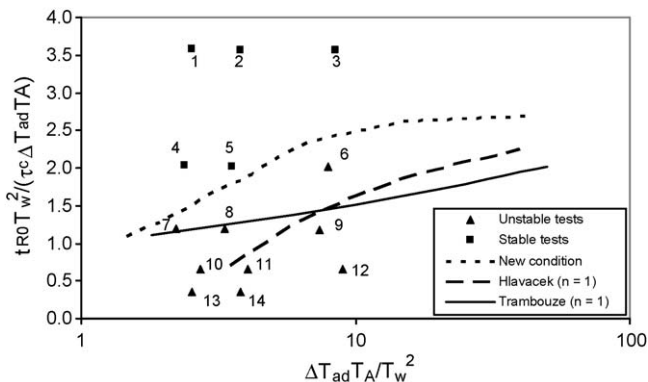
Fig. 5. Comparison of thermal stability criteria for first order reactions.

$$\frac{T_{\mathrm{w}}^2}{T_A \Delta T_{\mathrm{ad}}} \frac{t_{\mathrm{R0}}}{\tau_{\mathrm{c}}} > e^1 \left(\frac{T_A \Delta T_{\mathrm{ad}}}{T_{\mathrm{w}}^2} - 1 \right)$$

$$\times \left(1 - \left(\frac{T_A \Delta T_{\mathrm{ad}}}{T_{\mathrm{w}}^2} - 1 \right)^{-1/2} \right) \tag{24}$$

This relation is plotted in Fig. 5, which shows the stable and unstable experiments, and the experimental condition we established. The curve which represents the Hlavacek condition for first order reactions is below the experimental condition we established, and some unstable experiments can be regarded as stable by this condition (for example Experiment 6).

- Trambouze et al. [19] proposed a semi-empirical stability condition defined by the following expression:

$$\left(\frac{T_A \Delta T_{\mathrm{ad}}}{T_{\mathrm{w}}^2} \right)^{1.18} < \frac{t_{\mathrm{R0}}}{\tau_{\mathrm{c}}} \tag{25}$$

This condition, established for first order reactions, is largely used. The thermal stability condition is defined for initial conditions (t_{R0}), as most of the traditional stability conditions. However the rigorous condition ($T_A \Delta T_{\mathrm{ad}}/T_{\mathrm{w}}^2$) $\ll$ ($t_{\mathrm{R}}/\tau_{\mathrm{c}}$) should be checked throughout the reaction.

Trambouze's condition is presented in Fig. 5. This condition also under-estimates the experimentally observed thermal stability conditions: it supposes as stable some experiments which led to thermal runaways.

4.2.4. Discussion

Among the thermal stability conditions established for zeroth order reactions, that of Semenov is the most restrictive. Indeed Semenov considered an exothermic reaction system, in which no consumption of reactants could occur. The temperature of the reacting system could thus ultimately reach an infinite value in adiabatic mode. In the case of any reactant consumption, infinite values of the reactor temperature are not possible [15]. In the case where the parameter $\Delta T_{\mathrm{ad}} T_a/T_{\mathrm{w}}^2$ is below 100, Frank-Kamenetskii [20] proposes to take the consumption of reactant into account without fail, and modifies the Semenov criterion by the formula $Se = (1 + nX)/e$, where n is the reaction's order and X denotes conversion of a reactant. In our case, as the appar-

ent order of the reaction remains close to zero until conversion exceeds 90%, this correction is not necessary, but indicates that a thermal stability condition should not be defined for initial conditions only but verified throughout the reaction. Our experimental definition of thermal stability (see Section 4.1) is applied throughout the reaction, and implicitly takes consumption of the reactants into account.

Stability conditions are less restrictive for a first order reaction. Indeed the stability condition established for first order reactions (see Fig. 5, Hlavacek) is below the curve established for zeroth order reactions (see Fig. 4, Hlavacek). Indeed, for two different kinetics orders, having similar reaction enthalpy, initial reaction times and activation energies, the reaction rate with a higher order depends on the reactants concentrations. When reactants are consumed, their concentrations decrease, and the kinetics rate also decreases, what implies a less significant temperatures rises and thus less severe safety conditions.

For the experimentally studied system, the apparent peroxide hydrogen order lies between 0 and 2. At the beginning of the reaction, peroxide concentration is high, and the apparent kinetic order is very close to zero. Under these conditions, thermal explosion risk is significant (ΔT_{ad} is high) and our stability criterion leads to operating conditions which are more restrictive than that of Trambouze, even if these two criteria correspond to different kinetic orders. Moreover, our criterion is not based only on initial conditions, and has to be verified at every moment of the reaction. This characteristic is related to the complex kinetic expression in peroxide.

Morbidelli and Varma [3] proposed a semi-empirical stability condition, whose expression is presented below:

$$\frac{T_{\mathrm{w}}^2}{T_A \Delta T_{\mathrm{ad}}} \frac{t_{\mathrm{R0}}}{\tau_{\mathrm{c}}} > \lambda e^1 \left(1 - \left(\frac{\alpha_{\mathrm{c}}^0}{(T_A \Delta T_{\mathrm{ad}}/T_{\mathrm{w}}^2)} \right)^{2/3} \right) \tag{26}$$

with $\lambda = \dfrac{8.7}{7.66 + n^{0.6}}$, and :

$$\alpha_{\mathrm{c}}^0 = \frac{T_A}{2T_0} \left(\left(\frac{T_A}{T_0} - 2 \right) - \left(\frac{T_A}{T_0} \left(\frac{T_A}{T_0} - 4 \right) \right)^{0.5} \right) \tag{27}$$

Taking a zeroth order, λ is 1.136. For the varied initial temperatures α_{c}^0 lie between 1.10 and 1.11. Fixing this last value to 1.1, the Morbidelli's relation applied to our reactional system gives:

$$\frac{T_{\mathrm{w}}^2}{T_A \Delta T_{\mathrm{ad}}} \frac{t_{\mathrm{R0}}}{\tau_{\mathrm{c}}} > 1.136 e^1 \left(1 - \left(\frac{1.1}{(T_A \Delta T_{\mathrm{ad}}/T_{\mathrm{w}}^2)} \right)^{2/3} \right) \tag{28}$$

A correlation which is in very good agreement with the semi-experimental established condition (see Fig. 6) is then obtained.

Thus, none of the classical thermal stability condition can properly predict the stability of a process in case of variation of controls. The good agreement with a modified expression of the Morbidelli's condition surely characterizes the fact that the peroxide order remains close to zero on most of the reaction extent.
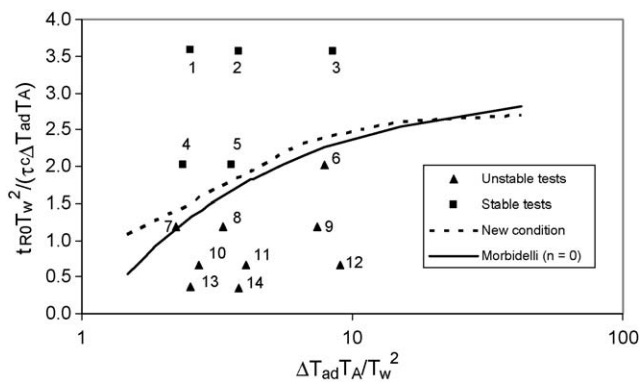
Fig. 6. Comparison with Morbidelli's condition.

4.3. Control of reaction

Experiments 5 and 6 (shown in Fig. 2), which have same initial temperatures and dichromate concentrations (and then same initial reaction rates) proceed in different ways. Indeed, at the beginning of the reaction, both act in the same (stable) way and the curves $T = f(t)$ have the same shape. Then Experiment 6 runs away, whereas Experiment 5 remains stable in case of variation of controls. For a better understanding of this phenomenon, a series of simulations for various initial peroxide concentrations was carried out.

Fig. 7a shows the variation of reaction temperature against time for different initial peroxide concentrations, and identical initial temperatures and dichromate concentrations. It can be noticed that the shape of the curves is the same on their first part. For low peroxide concentrations, reaction remains stable. When increasing this concentration, the temperature rise increases, and after a certain value (5.4 M), the curves present an inflection point, characteristic of a thermal runaway hazard in the case of breakdown of the exchanger or the cooling system. In the case of the so-called degenerate thermal explosion, when $\Delta T_{ad} T_A / T_w^2$ is between 4 and 10 (Frank-Kamenetskii [20]), overheat is relatively small, and transition from non-explosive to explosive processes proceeds very smoothly without any sharp change, which can also be clearly confirmed in Fig. 7a.
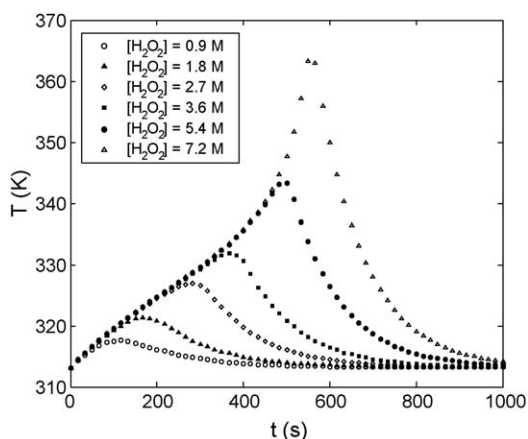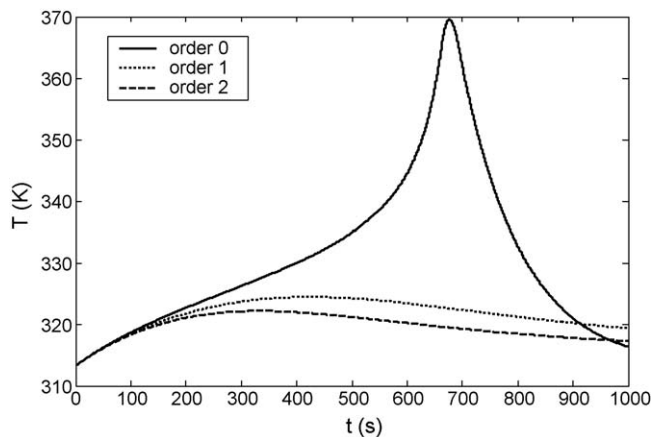

Fig. 8. Comparison of temperature variations for zeroth, first and second orders, $[H_2O_2] = 7.2$ M, $[Cr_2O_7] = 0.003$ M, $T_0 = 313$ K, $t_{R0}/\Delta T_{ad} = 30.8$ s K^{-1}.

Fig. 7b presents, on the diagram proposed by Villermaux [13] and Froment and Bischoff [14], the performed experiments and the thermal stability conditions as defined by various authors. Trambouze's condition supposes that all the experiments are carried out in a stable way, whereas the Semenov's condition considers all of them as unstable. The semi-empirical condition that we defined shows that the experiments for initial peroxide hydrogen concentrations lower than 3.6 M remain stable in case of variation of controls. This result is confirmed by the shape of the temperature reaction against time curves presented in Fig. 7a.

The studied reactional system is thus characterized by heat accumulation phenomena. The heat released by reaction involves a temperature rise, and therefore an increase in reaction rate, which is not balanced by a reduction of reactants concentrations.

For a better illustration of heat accumulation phenomena, a comparison between temperature profiles for fictive reactions of orders 0, 1 and 2 with same values of T_A, τ_c, T_w, $t_{R0}/\Delta T_{ad}$ is presented in Fig. 8. For these three profiles, the condition $(T_A \Delta T_{ad} / T_w^2) \ll t_{R0}/\tau_c$ is verified for initial conditions. It can be noticed that the first and second orders reactions do not induce

Fig. 7. Heat accumulation effect, $[Cr_2O_7] = 0.003$ M, $T_0 = 313$ K, $t_{R0}/\Delta T_{ad} = 30.8$ s K^{-1}.
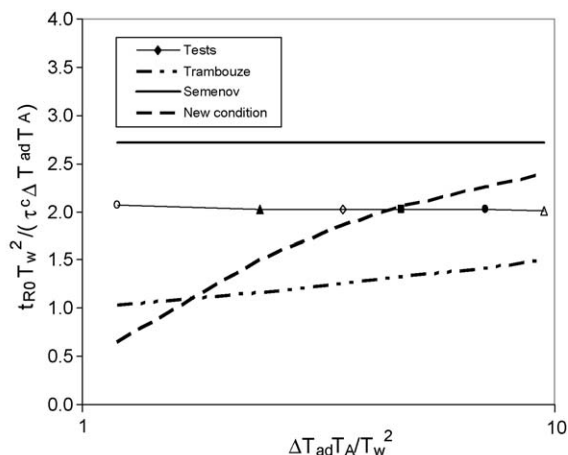
any thermal explosion, whereas the zeroth order reaction runs away.

For orders 1 and 2, the control of reaction can be thought of at its beginning. Indeed heat accumulation is not significant during the reaction, and consequently when reaction begins in a thermal stable way (absence of any initial inflexion point), thermal runaway cannot occur thereafter. On the contrary, for the particular case of zeroth order reactions the thermal stability condition should not apply for initial conditions only but have to be verified at every moment.

5. Conclusion

This work presents an experimental study dealing with stability conditions of a homogeneous catalytic chemical reaction. An experimental definition of the thermal stability conditions based on the in-line observation of the reactional temperature evolution has been proposed.

Using this stability criterion, it has been possible to study the stability conditions of a reactor with respect to thermal runaway, for the exothermic dichromate catalysed hydrogen peroxide decomposition. This runaway boundary has been specified in coupling experiments and simulations. We have demonstrated that none of the classical thermal stability conditions can properly predict the stability of a process in case of variation of controls, and that mathematical simulation remains the most universal method for analysis of such systems.

In general, as soon as the complex character of a reaction is established it is hard to expect that any of simplified analytical theory would be applicable. The system discussed in the paper is a good example. The reaction is complex—actually it is the multi-stage reaction, though for this specific case the model could be reduced to single equation which is different from traditional n-order model. In addition the system is essentially degenerate which complicates the analysis even more. Therefore it is quite understandable that most part of simple criteria verified here showed their inadequacy.

We have shown that the reactional system is characterized by significant heat accumulation phenomena where the heat released by reaction is not balanced by a reduction in kinetic rate. This characteristic imposes restrictive stability conditions which must be checked at every moment, and not only at the beginning of the reaction.

Appendix A. Evaporated flow

The evaporated mass flow can be expressed by the following expression:

$$F_{tot} = F_{O_2} + F_{H_2O} \tag{A.1}$$

Without any oxygen accumulation, the reaction stoichiometry gives:

$$F_{O_2} = rV/2$$

The mole number of peroxide in the reactional medium remains low compared to that of water. For example, for an initial peroxide concentration $[H_2O_2]_0$ of 1.8 M, the molar fraction of water x_{H_2O} is included between 0.97 at the beginning of reaction and 1 at the end. Thus, as a first approximation x_{H_2O} is supposed appreciably equal to 1.

The liquid–vapor equilibrium for water gives:

$$P_{H_2O} = y_{H_2O} P_{atm} = x_{H_2O} P_{H_2O}^{sat} \cong P_{H_2O}^{sat} \tag{A.2}$$

Since, the reaction is performed under atmospheric pressure:

$$P_{O_2} + P_{H_2O} = P_{O_2} + P_{H_2O}^{sat} = P_{atm} \tag{A.3}$$

In addition:

$$F_{H_2O} = y_{H_2O} F_{tot} = y_{H_2O}(F_{O_2} + F_{H_2O}) \tag{A.4}$$

From where:

$$F_{H_2O} = \frac{y_{H_2O}}{1 - y_{H_2O}} F_{O_2} \tag{A.5}$$

One finds finally:

$$F_{H_2O} = \frac{rV}{2} \frac{P_{H_2O}^{sat}}{P_{atm} - P_{H_2O}^{sat}} \tag{A.6}$$

For moderated peroxide concentrations, calculations according to Eq. (A.6) have shown that the mass of evaporated water during the reaction is low compared to the initial mass of water. For example, for $T = 333$ K and for an initial peroxide concentration of 1.8 M, the total mass of evaporated water represents 0.7% of the initial solution.

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